

D E C L A R A T I O N

In the matter of U.S. Patent  
Appln. Ser. No. 09/374,344  
in the name of TOTO LTD.

I, KONNO Akio, of Kyowa Patent and Law Office, 2-3,  
Marunouchi 3-Chome, Chiyoda-Ku, Tokyo-To, Japan, declare  
and say:

that I am thoroughly conversant with both the Japanese  
and English languages; and,

that the attached document represents a true English  
translation of Japanese Patent Application No. 7-326167  
filed on November 9, 1995.

I further declare that all statements made herein of  
my own knowledge are true and that all statements made on  
information and belief are believed to be true; and further  
that these statements were made with the knowledge that  
willful false statements and the like so made are punishable  
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Title of the Invention: METHOD OF RENDERING A MEMBER  
SURFACE HYDROPHILIC AND METHOD OF  
MAINTAINING HYDROPHILICITY

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SPECIFICATION

1. TITLE OF THE INVENTION

METHOD OF RENDERING A MEMBER SURFACE HYDROPHILIC AND METHOD OF MAINTAINING HYDROPHILICITY

2. CLAIMS

1. A method of rendering a member surface hydrophilic, comprising the steps of: forming on a substrate surface a mixed layer comprised of a siloxane resin (average composition formula:  $R^1_{4-n}SiO_{n/2}$  (where  $R^1$  is one kind of, or 2 kinds or more organic groups,  $1 < n < 4$ )) and titanium oxide; and irradiating thereon a UV.

2. A method of rendering a member surface hydrophilic, comprising the steps of: mixing titanium oxide particles with a composition comprised of a general formula of  $R^2_{4-n}Si(OR^3)_n$  (where  $R^2$  is one kind of, or 2 kinds or more organic groups, and  $R^3$  is one kind of, or 2 kinds or more alkyl groups, or hydrogen,  $0 \leq n < 4$ ); applying said mixture to a substrate; heat-curing thereof; and irradiating thereon a UV.

3. A method of rendering a member surface hydrophilic, comprising the steps of: mixing at least titanium oxide particles with a composition comprised of a general formula of  $R^4Si(OR^5)_3$  (where  $R^4$  is an organic group, and  $R^5$  is one kind of, or 2 kinds or more alkyl groups, or hydrogen); applying said mixture to a substrate; heat-curing thereof;

and irradiating thereon a UV.

4. A method of rendering a member surface hydrophilic, comprising the steps of: mixing silica particles with titanium oxide particles; further adding thereto a composition comprised of a general formula of  $R^4Si(OR^5)_3$  (where  $R^4$  is an organic group, and  $R^5$  is one kind of, or 2 kinds or more alkyl groups, or hydrogen); applying said addition to a substrate; heat-curing thereof; and irradiating thereon a UV.

5. A method of rendering a member surface hydrophilic, comprising the step of: irradiating a UV as necessary on the hydrophilic surface formed by claims 1 - 4.

[Detailed Description of the Invention]

[0001]

[Technical Field]

The present invention relates to a method of modifying a substrate surface to be rendered hydrophilic.

[0002]

[Prior Art]

Conventionally, there has been a method of forming a water-repellent resin film on a member surface to provide with stain resistance a member such as an exterior building material, sealant, sash, windowpane, automobile glass, mirror and solar battery cover, that is used outdoors exposed by rain; a member such as a bathroom mirror, wall material, floor material and ceiling, that is used in a water environment; and a member such as tableware and a

frying pan, that is cleaned with water.

[0003]

However, recently it has been apparent that, in a method of forming a water-repellent resin film like polytetrafluoroethylene on a substrate surface, a hydrophobic stain component is retained on a member after water is dried thereon, being noticeable ("Highpolymer", vol. 44, page 307 (1995)).

For example, a black, vertical pattern of stain produced on the external wall of a structural building is comprised of a hydrophobic substance like carbon black, a burned product (Scientific Lecture Summary of Japan Architecture Meeting, Oct. 1987), and is flown with flowing-down water onto the material surface to be generated (Construction Reports of Japan Architecture Meeting, No. 404, Oct. 1989). Therefore, when a material surface is painted with a general hydrophobic paint or a water-repellent paint, the above hydrophobic stain easily conforms to the material surface compared with water, so that the stain is hard to be washed off by rain, resulting in retention on the material surface, or being moved slightly to form a vertical pattern of stain.

[0004]

Based on the above facts, a method of applying a hydrophilic paint on an external wall has been suggested in order to avoid a black, vertical pattern of stain produced on the external wall of a structural building ("Highpolymer", vol. 44, page 307 (1995)).

Further, there has been a building material comprised of inorganic glass with a smooth surface like a glazed tile,

as a stain-resistant material. It is known that an inorganic glass material like a glazed tile is a hydrophilic material.

[0005]

[Problems to be Solved by the Invention]

However, an acrylic silicon resin, water-base silicon coating agent, graft polymer of silicon and acrylic resins, block polymer of silicon and acrylic resins, acrylic resin, and acrylic-styrene resin, that are hydrophilic paints used conventionally, have a contact angle with water of the order, at most, of  $70^\circ$  as an initial value; the angle is of the order, at most, of  $50^\circ$ , although the materials exposed to rain allow the hydrophilicity to be improved a little within several months. For that reason, it is hard to prove that a sufficient effect works in stain resistance. Also, initially the angle of  $70^\circ$  or more with hydrophobicity causes stains so often; and it takes several months for hydrophilization to about  $50^\circ$ . After all, a stain-resistant effect by weak hydrophilicity can be obtained after that.

[0006]

Also, a building material comprised of inorganic glass with a smooth surface like a glazed tile, shows a favorable result of a contact angle with water of about  $5 - 20^\circ$  at production; but as time passes, a component such as lower carboxylic acid and surfactant, including both of a hydrophilic functional group and a hydrophobic functional group adheres to the material surface to render thereof hydrophobic. ("Design of Glass Surface" by Kindai Henshusha (1983)). Therefore, low hydrophilicity cannot be maintained for a long period to be deteriorated to about

30 - 50°. For that reason, the material can be expected to have a stain-resistant effect slightly better than that of the above paints, but it is hard to say it works a sufficient effect.

[0007]

In view of the above facts, the present invention offers a method of rendering a member hydrophilic, so that the member can be rendered super-hydrophilic to a contact angle with water of less than 5°, and can maintain the hydrophilicity as long as subjected to irradiation of a UV as necessary.

[0008]

[Means to be Solved by the Invention and effect thereof]

In order to solve the above problems, the present invention offers a method of rendering a member surface hydrophilic, comprising the steps of: forming on a substrate surface a mixed layer comprised of a siloxane resin (average composition formula:  $R^1_{4-n}SiO_{n/2}$  (where  $R^1$  is one kind of, or 2 kinds or more organic groups,  $1 < n < 4$ )) and titanium oxide; and irradiating thereon a UV.

[0009]

In the preferable embodiment of the present invention, a method of rendering a member surface hydrophilic is comprised of the steps of: mixing titanium oxide particles with a composition comprised of a general formula of  $R^2_{4-n}Si(OR^3)_n$  (where  $R^2$  is one kind of, or 2 kinds or more organic groups, and  $R^3$  is one kind of, or 2 kinds or more alkyl groups, or hydrogen,  $0 \leq n < 4$ ); applying said mixture to a substrate; heat-curing thereof; and irradiating



thereon a UV.

[0010]

In the preferable embodiment of the present invention, a method of rendering a member surface hydrophilic is comprised of the steps of: mixing at least titanium oxide particles with a composition comprised of a general formula of  $R^4Si(OR^5)_3$  (where  $R^4$  is an organic group, and  $R^5$  is one kind of, or 2 kinds or more alkyl groups, or hydrogen); applying said mixture to a substrate; heat-curing thereof; and irradiating thereon a UV.

[0011]

In the preferable embodiment of the present invention, a method of rendering a member surface hydrophilic is comprised of the steps of: mixing silica particles with titanium oxide particles; further adding thereto a composition comprised of a general formula of  $R^4Si(OR^5)_3$  (where  $R^4$  is an organic group, and  $R^5$  is one kind of, or 2 kinds or more alkyl groups, or hydrogen); applying said addition to a substrate; heat-curing thereof; and

[0012]

In the preferable embodiment of the present invention, a method of rendering a member surface hydrophilic is comprised of the step of: irradiating a UV as necessary on the hydrophilic surface formed by the above methods.

[0013]

A method of rendering a member surface hydrophilic is comprised of the steps of: forming on a substrate surface a mixed layer comprised of siloxane resin and titanium oxide; and irradiating thereon a UV, so that the photo oxidative action of titanium oxide in irradiating a UV, allows an

organic group  $R^6$  on the substrate surface to be decomposed without affecting the Si-O bond in the siloxane resin, and then a Si- $R^6$  bond to be changed into a Si-OH bond (Fig. 1). This will provide super-hydrophilicity.

Also, upon subjecting to a UV as necessary, as time passes, the hydrophilicity can be maintained in an environment where a component such as lower carboxylic acid and surfactant, including both of a hydrophilic functional group and a hydrophobic functional group adheres to the material surface; this reason is considered to be due to the mechanism as follows. First, it is assumed that a component including both of a hydrophilic group and a hydrophobic group adheres to the top of the above Si-OH bond. At this point, moisture in the air and a hydroxide ion exist in the surroundings. The hydrophilic functional group absorbed on the top of the Si-OH bond, is easily eliminated by an electron or hole generated from the photo semiconductor action of titanium oxide. However, since the Si-OH bond has strong hydrophilicity, the hydrophilic functional group is easily absorbed on the top thereof. Then, a component including both of a hydrophilic functional group and a hydrophobic functional group, moisture in the air and hydroxide ion, are absorbed. However, a component comprised only of a hydrophilic function group such as moisture in the air and hydroxide ion, is easily absorbed compared with the component including a hydrophilic functional group and a hydrophobic functional group. Such removal is repeated, so that a large amount of the components comprised only of a hydrophilic functional group such as moisture in the air and hydroxide ion, is absorbed for an increasing proportion of

only these absorbed components. In this way, both actions of the photo semiconductor of titanium oxide and Si-OH hydrophilic surface, can maintain hydrophilicity.

[0014]

[Embodiment of the Invention]

The basic steps of the present invention are explained below.

First, a mixed layer comprised of a siloxane resin (average composition formula:  $R^1_{4-n}SiO_{n/2}$  (where  $R^1$  is one kind of, or 2 kinds or more organic groups,  $1 < n < 4$ )) and titanium oxide, is formed on a substrate surface.

The  $R^1$  is an organic group; e.g. an alkyl group such as methyl, ethyl and propyl groups, and an aryl group such as phenyl group, can be used.

Also, any substrate material such as a metal, inorganic material, resin and composite thereof (enamel, steel plate panel, decorative plywood and building material painted or plated thereon), can be used.

[0015]

In forming on a substrate surface a mixed layer comprised of a siloxane resin (average composition formula:  $R^1_{4-n}SiO_{n/2}$  (where  $R^1$  is one kind of, or 2 kinds or more organic groups,  $1 < n < 4$ )) and titanium oxide, one kind of, or 2 kinds of more raw materials that can form a siloxane resin with cured reaction and a titanium oxide source, are applied to the substrate to generate a siloxane resin with cured reaction.

[0016]

In one kind of the raw material that can form a siloxane resin with cured reaction, e.g.  $R^2_{4-n}Si(OR^3)_n$

(where  $R^2$  is one kind of, or 2 kinds or more organic groups, and  $R^3$  is one kind of, 2 kinds or more alkyl groups or hydrogen,  $0 \leq n < 4$ ), can preferably be used. Also, in 2 kinds of the materials, e.g. a multiple kind  $R^2_{4-n}Si(OR^3)_n$  with different ns, or silica and  $R^2_{4-n}Si(OR^3)_n$ , can be used. After hydrolysis by heating, the materials in both cases are polymerized with dehydrated-condensation reaction to generate a siloxane resin.

[0017]

The titanium oxide source refers to a raw material that can generate a titanium oxide crystal at completion of the final step. For example, an anatase-form titanium oxide sol and anatase-form titanium oxide powder, can be used.

[0018]

To apply the material to a substrate, can include the methods of: applying on the substrate a mixture of a raw material that can form a siloxane resin with cured reaction and a titanium oxide source; applying on the substrate a liquid wherein said mixture is dispersed; or immersing the substrate in this dispersed liquid. The second one of these methods is easy.

[0019]

The cured reaction to generate a siloxane resin, is made by thermosetting or leaving to stand at room temperature. Of these, the thermosetting is convenient, because it permits curing at the order of 100 - 300°C for a short time. Also, the curing by leaving to stand at room temperature is safe and preferable for spray application at a site.

[0020]

Irradiating a UV may use a light source that can irradiate a UV light at the final producing step.

Also, a member such as an exterior building material, sealant, sash, windowpane, automobile glass, mirror and solar battery cover, that is used at a place in a sunray, is subjected to a sunray UV after application. Such case is applied to this step.

Further, a member such as a bathroom mirror, wall material, floor material and ceiling, that is used at a place in indoor illumination, is also subjected to an indoor illumination UV after application. Such case is also applied to this step.

Furthermore, a member such as tableware, that is stored in an unused condition for a constant period, can be subjected to a UV light source during storage. Such case is also applied to this step.

[0021]

A member made in the above step, can maintain hydrophilicity by UV irradiation as necessary. This allows stain resistance to be maintained on a semipermanent basis.

The term "as necessary" refers to irradiating a light in the condition where a member is left after a UV irradiation to be rendered hydrophilic at being subjected to the UV again. Such irradiation is sufficient in the case where the a UV reaches a mixed layer comprised of a siloxane resin (average composition formula:  $R^1_{4-n}SiO_{n/2}$  (where  $R^1$  is one kind of, or 2 kinds or more organic bases,  $1 < n < 4$ )) and titanium oxide. The critical time is not apparent at present. Although the member left outdoors is hardly

subjected to a UV at night, it maintains its hydrophilicity and stain resistant for a long period, as described later. Therefore, the member may be subjected to UV irradiation on at least half-day basis.

[0022]

[Example]

Example 1 (hydrophilization by a sunray, sol)

The silica in a silica sol (Glaska A of Japan Synthetic Rubber Co.) and trimethoxymethylsilane (Glaska B of Japan Synthetic Rubber Co.), were mixed at a ratio by weight of 3 : 1, and then the liquid with the whole solute concentration of 20 % by weight was applied to a 10-cm square aluminum substrate. After that, the substrate was rendered thermosetting at 150°C to form a resin layer with a 5  $\mu$  m film thickness (sample A).

The silica sol was added to an anatase-form titanium oxide sol with an average particle diameter of 0.01  $\mu$  m (solute concentration of 10% by weight, nitric-acid dispersed type, pH 0.8), and then, the solution was diluted with ethanol, to which the trimethoxymethylsilane is added, and was applied onto the sample A. After that, the sample was rendered thermosetting at 150°C to form a mixed layer with a 0.1  $\mu$  m film thickness (sample S). The ratio by weight of the titanium oxide solid content versus the sum of the solid content of the silica and trimethoxymethylsilane (resin) and the titanium oxide solid content in the mixed layer, was 50%.

[0023]

The sample S, for the purposes of comparison, the sample A, and sample B wherein a silicon resin is applied to

a calcium silicate plate, were placed in the sample mounted part of the apparatus shown in Fig. 2. Then, the apparatus was left on the roof of a 5-story building, to evaluate hydrophilic degrees as time elapses. The hydrophilic degree was evaluated with a contact angle with water on the sample surface.

[0024]

As a result, before being left in a sunray, the sample S showed  $80^\circ$ ; the comparing sample A,  $90^\circ$ ; and the comparing sample B,  $70^\circ$ . Being left for one day, the degree of the sample S was changed to  $0^\circ$ , while that of the comparing sample A was  $90^\circ$ , and that of the comparing sample B was  $80^\circ$ , which were hardly changed. The above fact revealed that the sample according to the present invention is rendered super-hydrophilic to  $0^\circ$  by sunray irradiation for a short time of about one day.

[0025]

Example 2 (hydrophilicity and stain-resistance maintaining effect of the above samples) The sample S, comparing samples A and B made in Example 1 were further left for a long time, to evaluate, as time elapses, a hydrophilic change and adhesion of a black, vertical pattern of stain. The time-varying change in adhesion of a black, vertical pattern of stain, was evaluated by a difference in color difference depending on a visual check and place in the same sample (a difference in color difference between a much stain part (a part with a vertical pattern of stain) and a less stain part (a part without a vertical pattern of stain)) The color difference for a standard sample (a sample before being subjected to a sunray) was measured with a

color difference meter.

Further, the specific glossiness for a sample before being subjected to a sunray was found with a glossiness meter. The incidence angle was 60°.

[0026]

The time-varying change in a hydrophilic change is shown in Fig. 3. The diagram showed that all the samples that were left for a long period improved the hydrophilicity. However, the comparing samples A and B left for 10 months were only rendered hydrophilic to about 40 - 50°. On the contrary, the degree of the sample S left for one day reached 0°, which was maintained for 10 months, showing an excellent super-hydrophilicity maintaining effect. Also, as described above, this shows that the hydrophilicity can be maintained for a long period, although the sample was hardly subjected to a UV at night, and suggests that the hydrophilic maintaining effect can be delivered in this embodiment sample without being constantly subjected to a UV.

[0027]

Also, the adhesion of a black, vertical pattern of stain one week later is shown in Fig 4; and that one month later, in Fig. 5. In the diagrams, the width of color difference data shows the color difference between a part without a vertical pattern of stain and a part with a vertical pattern of stain. In other words, this width shows the contrast of a vertical pattern of stain. Also, the minimum value of the color difference data shows adhesion of a part without a vertical pattern of stain.



[0028]

In Fig. 4, one week later, a vertical pattern of stain of contrast corresponding to the color difference width of 3 in the comparing samples A and B, was already observed. In the embodiment sample, the width was less than 1, and a vertical pattern of stain was not observed visually. Also, the width of the adhesion of the part without a vertical pattern of stain was held within 1 in all the samples, and the embodiment sample had the most favorable result.

[0029]

Also, in Fig. 5, one month later, a vertical pattern of stain of contrast corresponding to the color difference width of 3 in the comparing sample A, and that of 5 in the comparing sample B, were already observed. In the embodiment sample, the width was less than 1, and a vertical pattern of stain was not observed visually. Also, the embodiment sample had the most favorable result in the adhesion of the part without a vertical pattern of stain, that was held within 1.

[0030]

A change in the glossiness ratio by outdoor leaving is shown in Fig. 6. According to the diagram, 3 months later, the glossiness ratio was lowered to 0.52 in the comparing sample A; the ratio was a favorable result of 0.95 or more in the embodiment sample.

[0031]

Example 3 (hydrophilization by a BLB)

In a manner similar to Example 1, a mixed layer with a 0.1  $\mu$ m film thickness was formed on an aluminum substrate. The ratio by weight of the titanium oxide solid content

versus the sum of the solid content of the silica and trimethoxymethylsilane (resin) and the titanium oxide solid content in the mixed layer, was altered variously.

The above mixed layer formation was subjected to a 0.5 mW/cm<sup>2</sup> BLB lamp, to measure the time-varying change in a contact angle with water, wear resistance, and surface hardness.

[0032]

In the wear-resistant test, slided wearing with a plastic eraser was performed, and changes in an appearance were compared for evaluation.

The evaluating references are shown below.

- ◎: No change in 40 reciprocated slidings.
- : 10 or more and less than 40 slidings caused a surface layer to be scratched and peeled off.
- △: 5 or more and less than 10 slidings caused a surface layer to be scratched and peeled off.
- ×: Less than 5 slidings caused a surface layer to be scratched and peeled off.

The surface hardness was evaluated with a hardness wherein a member surface was scratched with a pencil with different hardnesses of 6B - 9H to produce scoring.

[0033]

The typical results with respect to a time-varying change in a contact angle with water are shown in Fig. 7. In Fig. 7, all the samples were rendered super-hydrophilic to 0° within 200 hours by being subjected to a 0.5 mW/cm<sup>2</sup> BLB lamp. Therefore, it was apparent that at least 5 % or more titanium oxide by weight can realize super-hydrophilization.

[0034]

The typical result with respect to wear resistance when the weight of the titanium oxide in the mixed layer was changed, is shown in Fig. 8. According to the diagram, the titanium oxide of 90% or less by weight showed a favorable result of ©.

The typical result with respect to surface hardness when the weight of the titanium oxide in the mixed layer was changed, is shown in Fig. 9. According to the diagram, although the layer was made of an soft, aluminum substrate, the hardness of the titanium oxide of 90% or less by weight was 5B; and that of the titanium oxide of 60% or less by weight was H or more. Thus, it was evident that a rather hard film can be made.

[0035]

Example 4 (storage implement + cleaning facility)

In a manner similar to Example 1, a mixed layer with a  $0.1 \mu\text{m}$  film thickness was formed on an aluminum substrate. The ratio by weight of the titanium oxide solid content versus the sum of the solid content of the silica and trimethoxymethylsilane (resin) and the titanium oxide solid content in the mixed layer, was 50%.

The above sample was placed in a box containing a BLB lamp, and was subjected to a  $0.3 \text{ mW/cm}^2$  irradiation to be left for 3 hours.

[0036]

After that, the above sample was taken out, and further was subjected to the oleic acid in a dropper to be left for 5 minutes. Then, this sample was immersed in the water such that the member was horizontal. The contact angle with

oleic acid was increased to form a droplet which was floated up soon. It is thought that the reason why this phenomenon occurred was that the sample surface was rendered super-hydrophilic, allowing water molecules that conform to the sample surface far more easily than the oleic acid to be burrowed between the sample surface and oleic acid in the water.

[0037]

In the above result, for example, it is considered that if there is a tableware storage box with a light source irradiating a UV, oil stains on the surface of tableware rendered hydrophilic with the above method will be cleaned easily simply by sinking the tableware in the water. Further, if this method can clean oil stains on the surface of tableware, it will need no neutral detergent and help prevention of water pollution.

[0038]

Also, for the purposes of comparison, the comparing samples A and B shown in Example 1 were subjected to the oleic acid to be left for 5 minutes. Then, a test wherein these samples were immersed in the water so that the member was horizontal, was conducted. However, the oleic acid was not floated up unlike the above embodiment sample. Besides it, oil scrubbed with fingers remained to be spreaded on the sample surfaces.

[0039]

Example 5 (hydrophilization by a BLB, no silica sol in a mixed layer) In a manner similar to Example 1, first a resin layer was formed on an aluminum substrate. The trimethoxymethylsilane (Glaska B of Japan Synthetic Rubber

Co.), was added to an anatase-form titanium oxide sol with an average particle diameter of  $0.01 \mu\text{m}$  (solute concentration of 10 % by weight, nitric-acid dispersed type, pH 0.8), and then, the solution was diluted with ethanol, and applied onto the above resin layer. After that, the layer was rendered thermosetting at  $150^{\circ}\text{C}$  to form a mixed layer with a  $0.1 \mu\text{m}$  film thickness. The ratio by weight of the titanium oxide solid content versus the sum of the solid content of the silica and trimethoxymethylsilane (resin) and the titanium oxide solid content in the mixed layer, was 50 %.

The above mixed layer formation was subjected to a  $0.5 \text{ mW/cm}^2$  BLB lamp, to measure a contact angle with water one day later. Consequently, it was rendered super-hydrophilic to  $0^{\circ}$ .

[0040]

#### Example 6 (effect of film thickness)

In a manner similar to Example 1, a mixed layer was formed on an aluminum substrate. However, the film thickness of the mixed layer was altered variously. The ratio by weight of the titanium oxide solid content versus the sum of the solid content of the silica and trimethoxymethylsilane (resin) and the titanium oxide solid content in the mixed layer, was 50 %. The above mixed layer formation was subjected to a  $0.5 \text{ mW/cm}^2$  BLB lamp, to measure the time-varying change in a contact angle with water.

[0041]

The results are shown in Fig. 10. According to the diagram, in the experimented film thickness of at least  $0.03 \mu\text{m} - 2.5 \mu\text{m}$ , all the samples were rendered super-

hydrophilic to 0° within 50 hours. Also, it was apparent that, the time required for super-hydrophilization of a thin film of less than 0.6  $\mu\text{m}$  is shorter than that of a thick film of 2.5  $\mu\text{m}$ .

[0042]

[Effect of the Invention]

A method of rendering a substrate surface hydrophilic is comprised of the steps of: forming on the substrate surface a mixed layer comprised of a siloxane resin (average composition formula:  $\text{R}^1_{4-n}\text{SiO}_{n/2}$  (where  $\text{R}^1$  is one kind of, or 2 kinds of more organic groups,  $1 < n < 4$ ) and titanium oxide; and irradiating thereon a UV, so that the substrate surface can be rendered super-hydrophilic to a contact angle with water of less than 5°, and maintain the hydrophilicity as long as subjected to irradiation of a UV as necessary.

[Brief Description of the Drawings]

Fig. 1

It is a diagram showing a chemical change in the step of irradiating a UV according to the present invention.

Fig. 2

It is a diagram showing an outdoor leaving test apparatus of the embodiment according to the present invention (the length unit is millimeter).

Fig. 3

It is a diagram showing the hydrophilicity maintaining characteristic at outdoor leaving of the embodiment according to the present invention.

Fig. 4

It is a diagram showing the stain resistance at outdoor

leaving for one week of the embodiment according to the present invention.

Fig. 5

It is a diagram showing the stain resistance at outdoor leaving for one month of the embodiment according to the present invention.

Fig. 6

It is a diagram showing the maintaining characteristic of glossiness ratio at outdoor leaving of the embodiment according to the present invention.

Fig. 7

It is a diagram showing the hydrophilic degree at BLB lamp irradiation of the embodiment according to the present invention.

Fig. 8

It is a diagram showing the relation between the ratio by weight of titanium oxide and wear resistance in a mixed layer of the embodiment according to the present invention.

Fig. 9

It is a diagram showing the relation between the ratio by weight of titanium oxide and surface hardness in a mixed layer of the embodiment according to the present invention.

Fig. 10

It is a diagram showing the relation between film thickness and hydrophilic degree in a mixed layer of the embodiment according to the present invention.

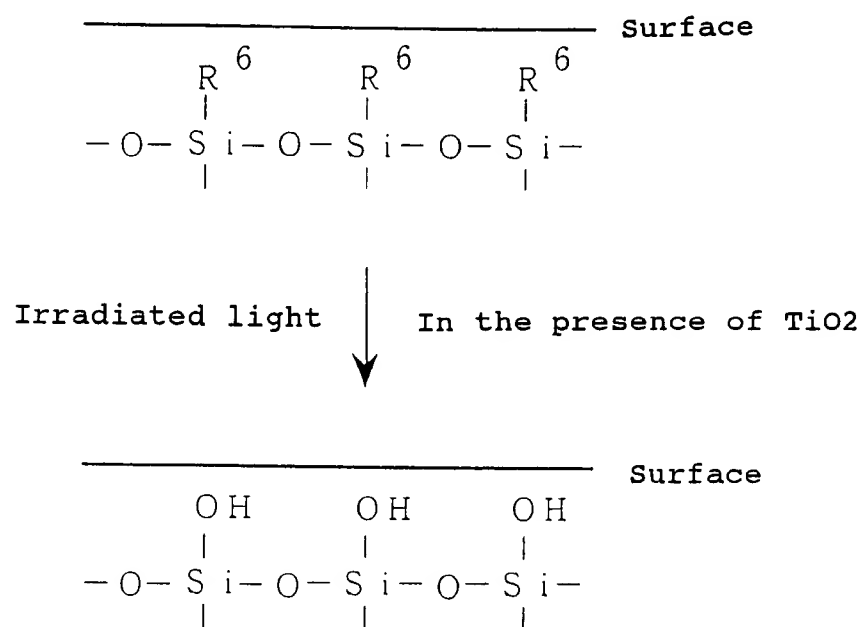
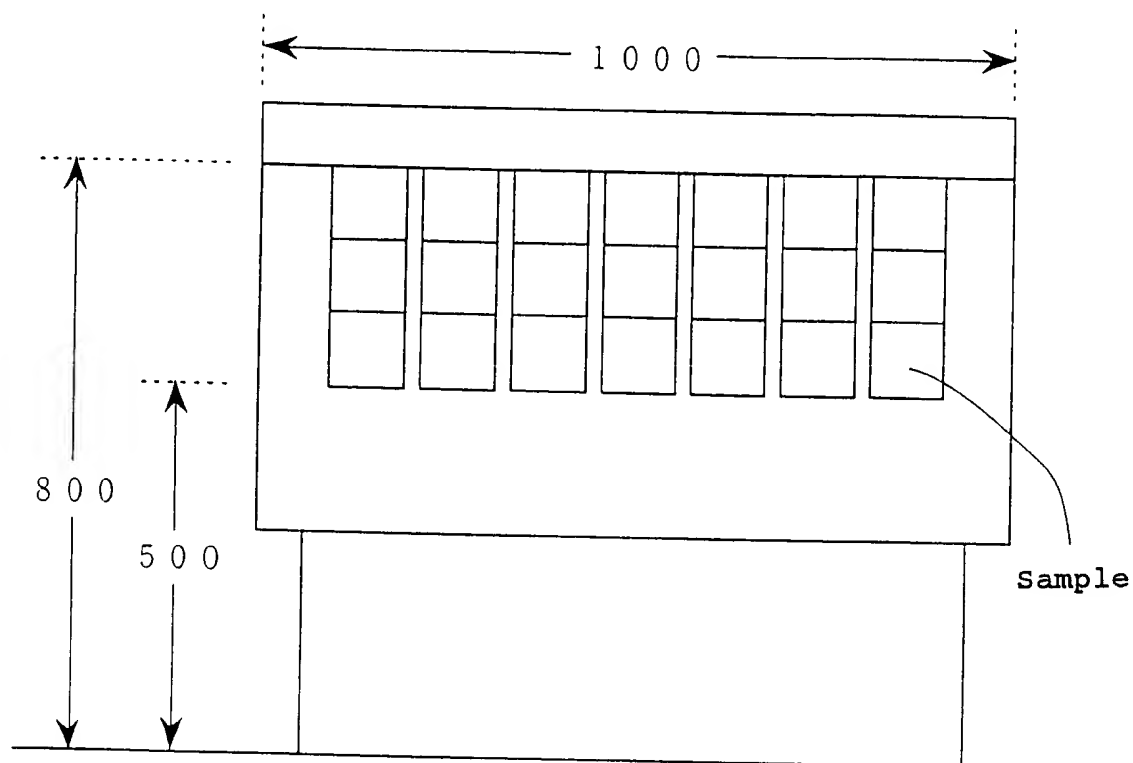
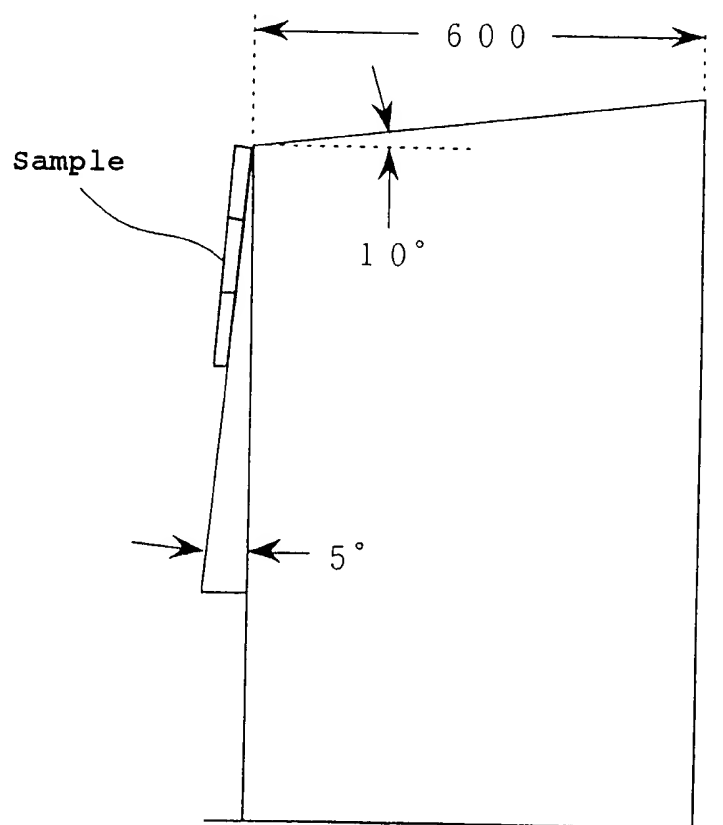


Fig. 1





Front view



Side view

Fig. 2

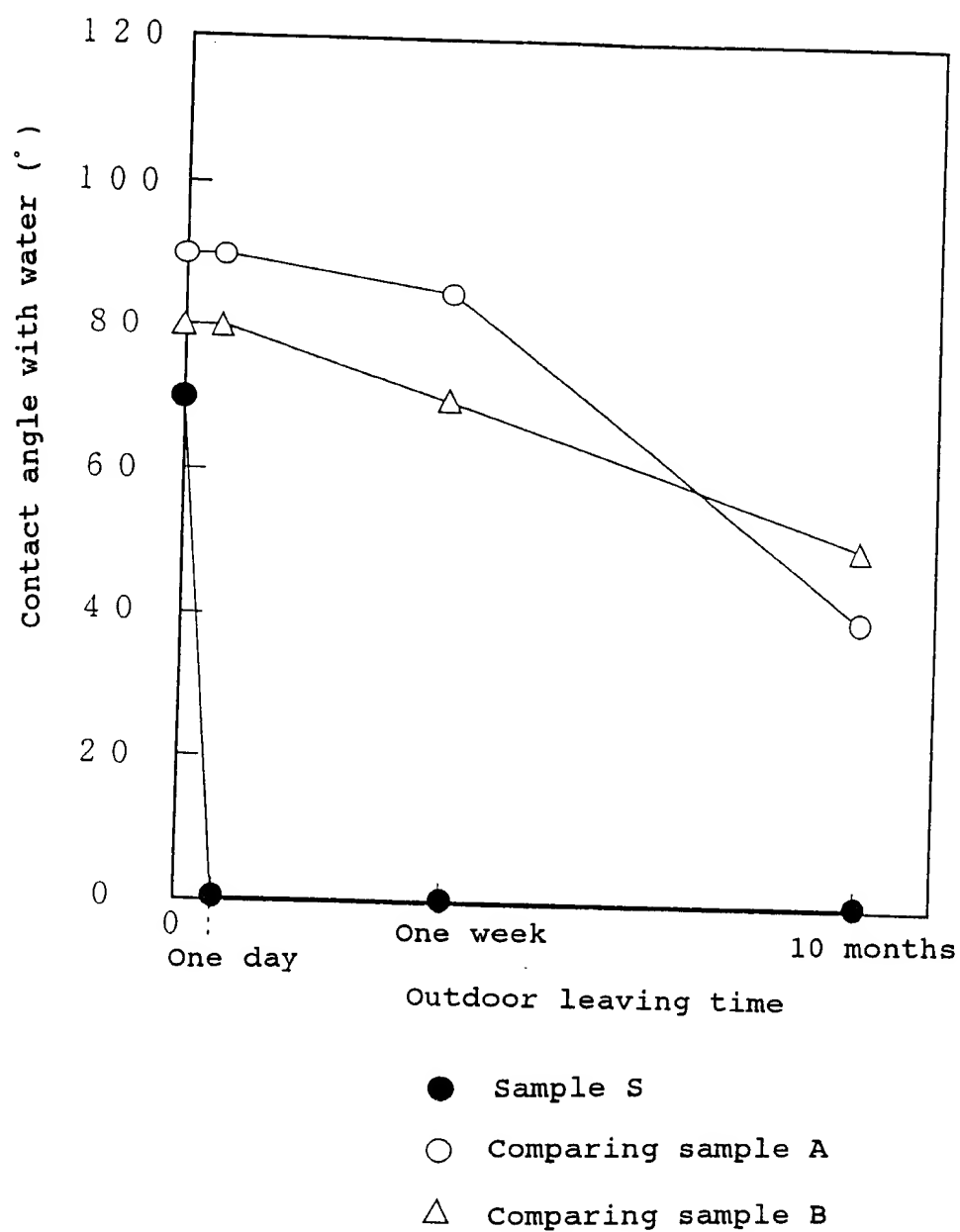


Fig. 3

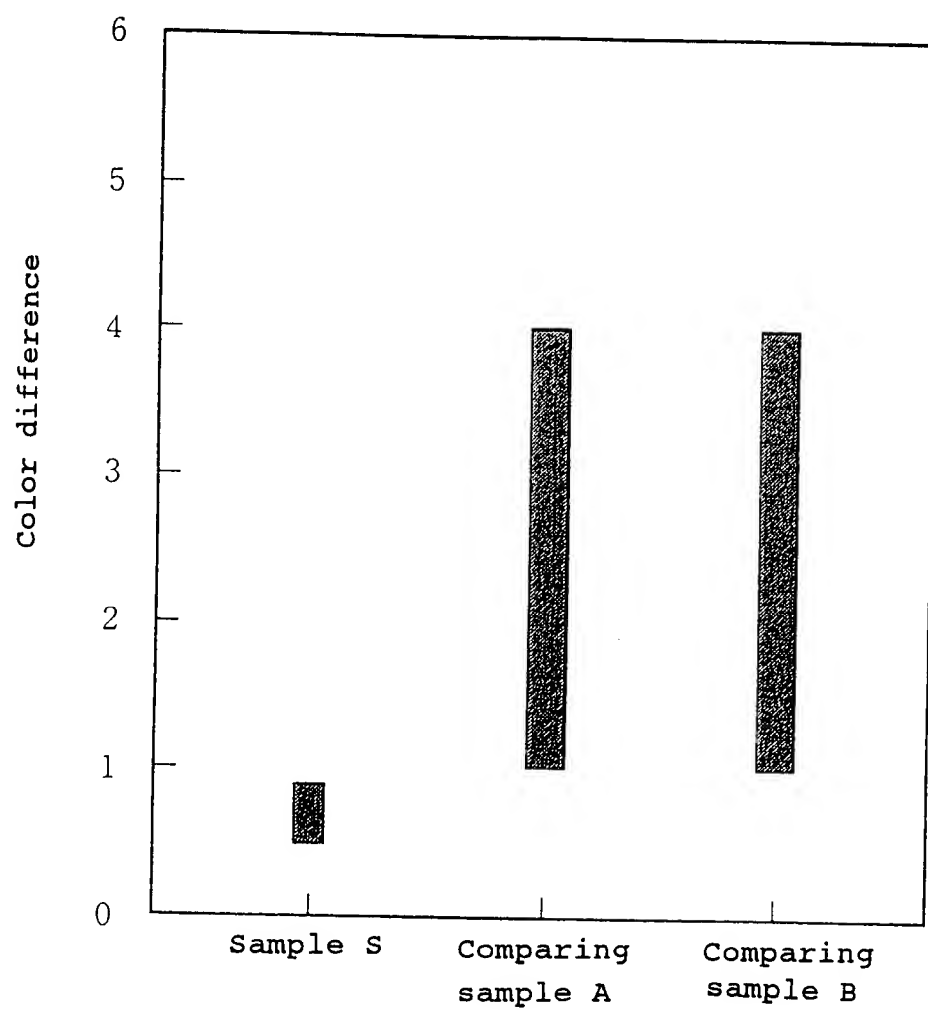


Fig. 4

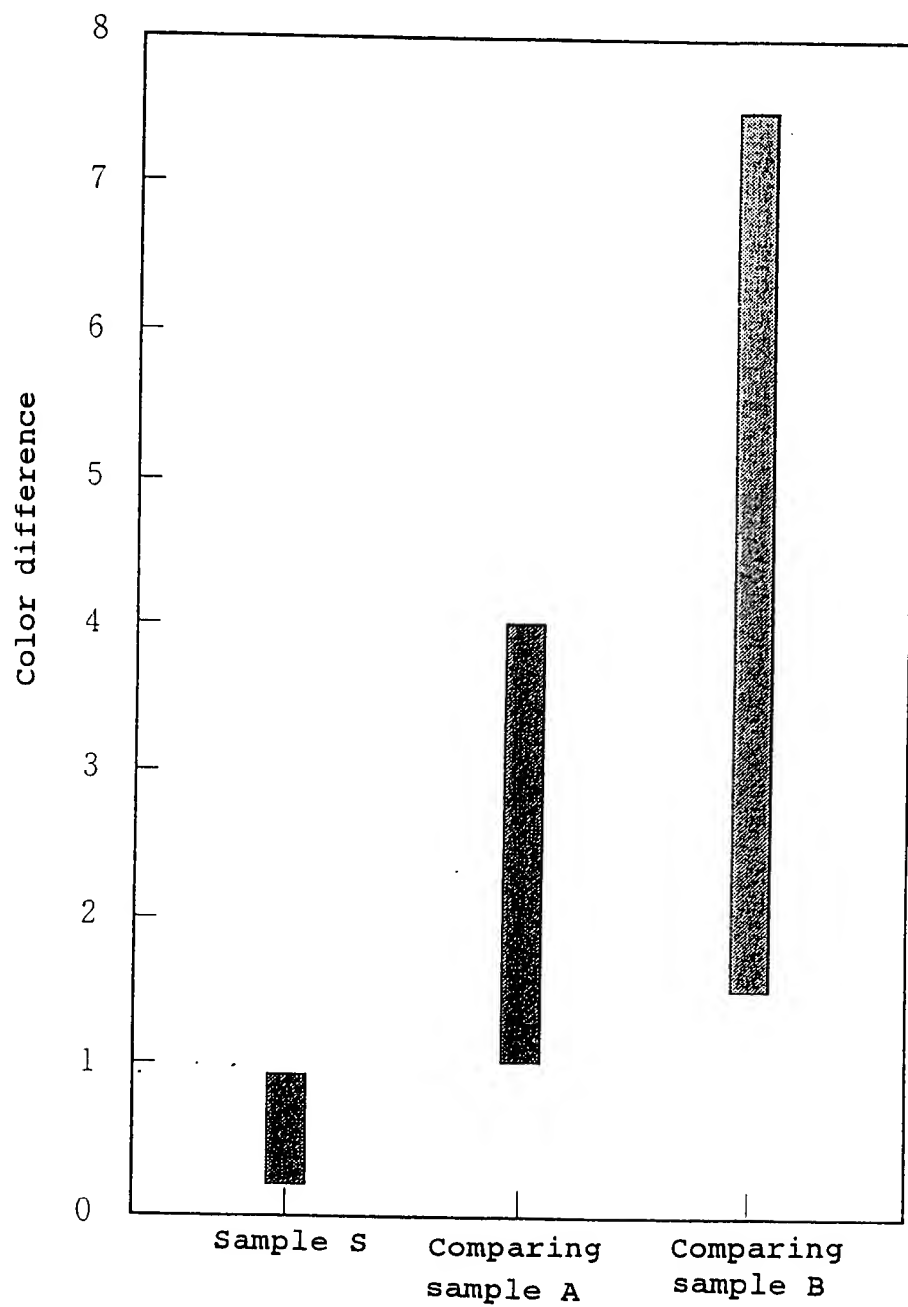


Fig. 5

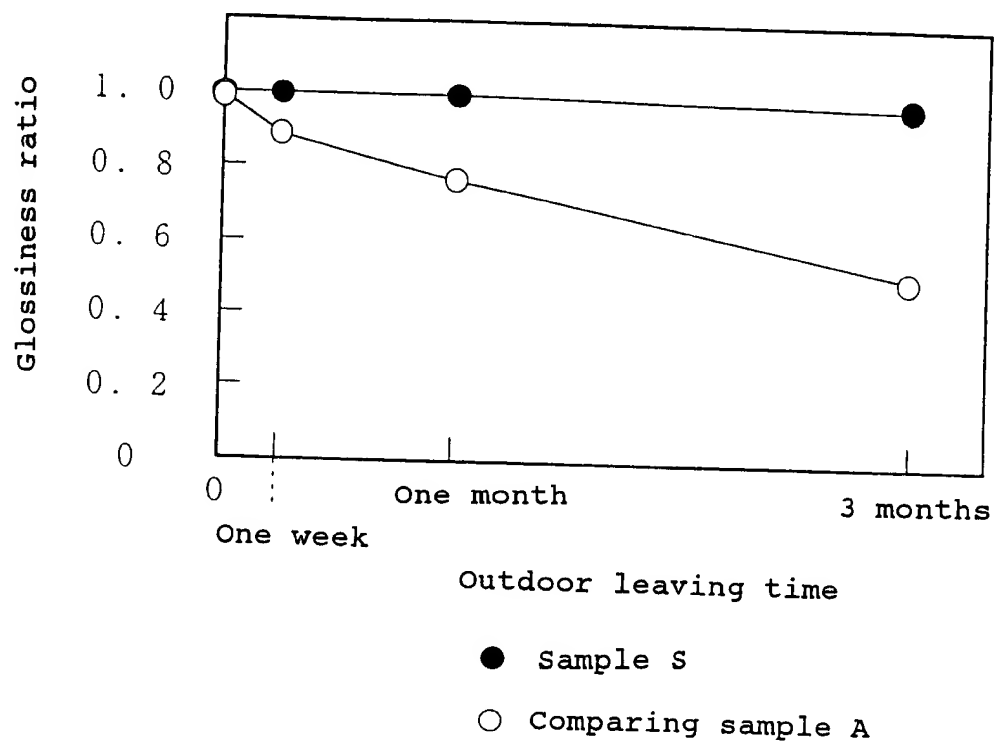


Fig. 6

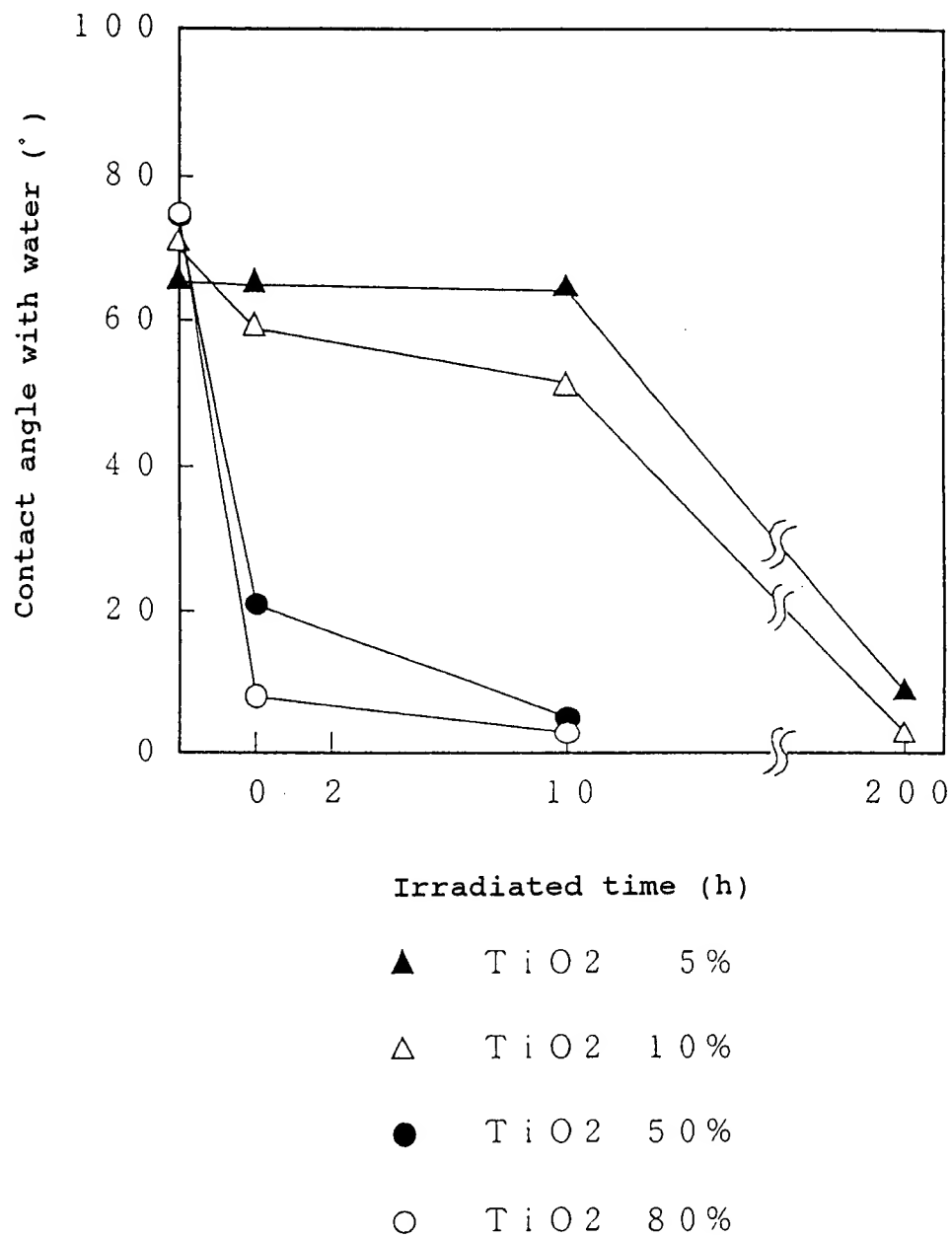


Fig. 7

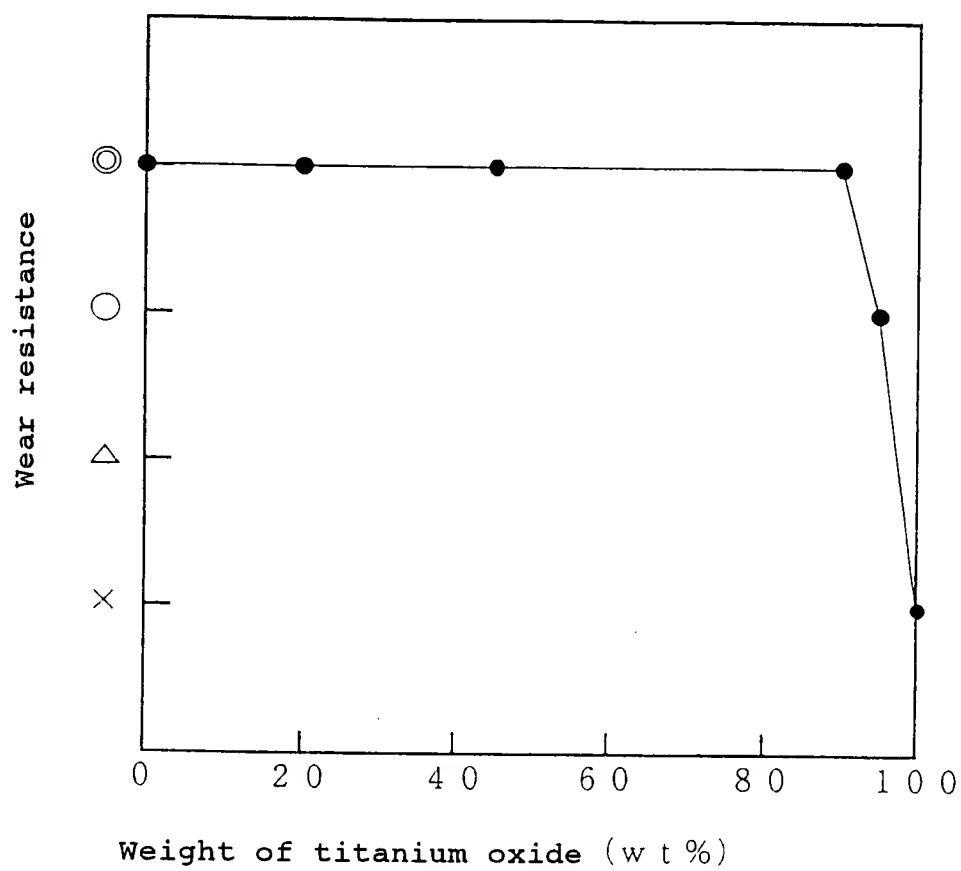


Fig. 8

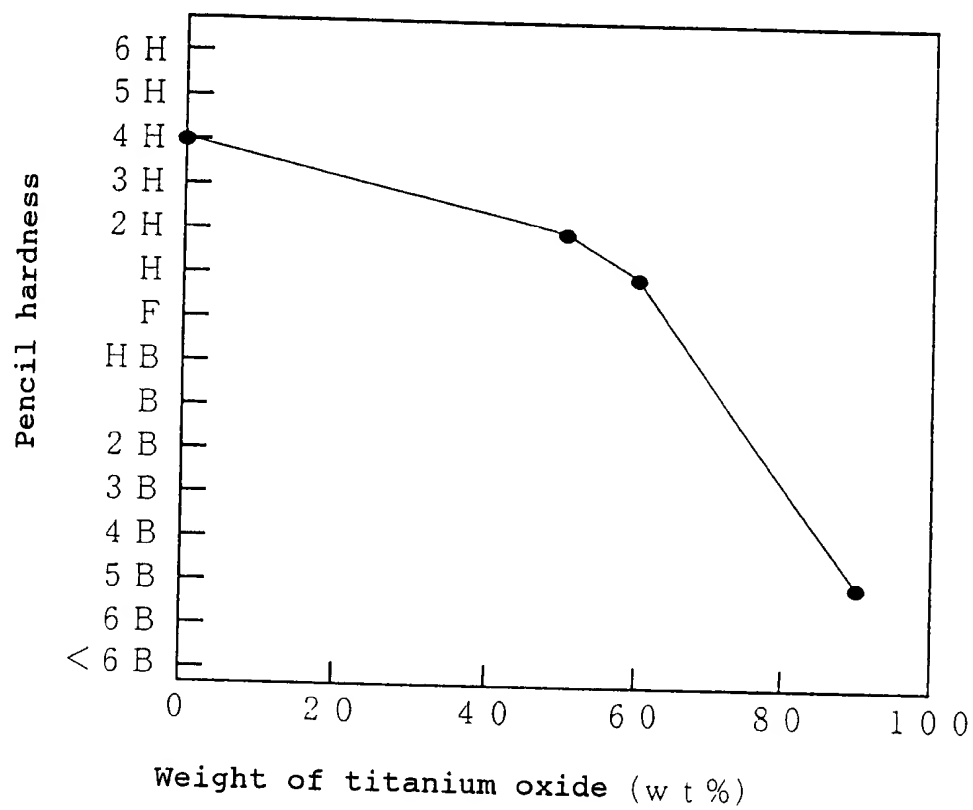
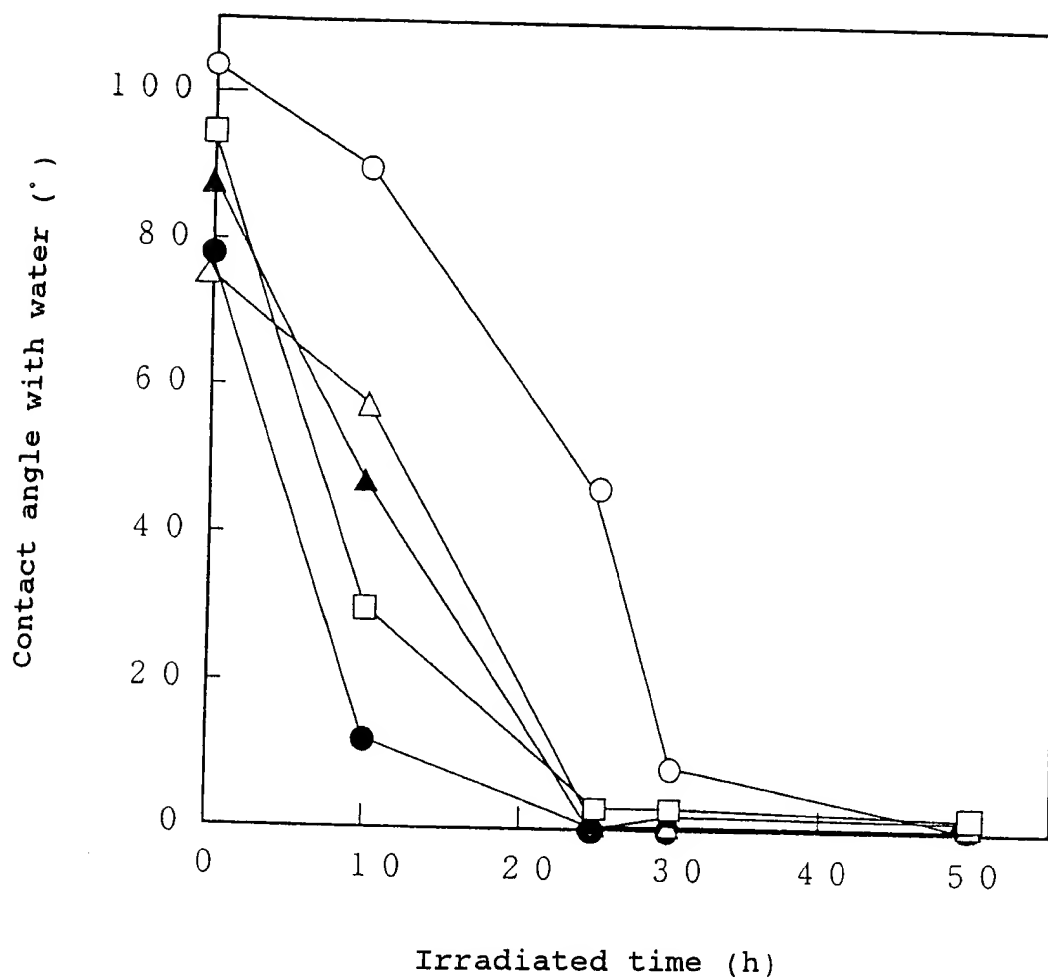


Fig. 9





- Film thickness of a mixed layer 2.5  $\mu\text{m}$
- △ Film thickness of a mixed layer 0.6  $\mu\text{m}$
- Film thickness of a mixed layer 0.2  $\mu\text{m}$
- ▲ Film thickness of a mixed layer 0.1  $\mu\text{m}$
- Film thickness of a mixed layer 0.03  $\mu\text{m}$

Fig. 10

## ABSTRACT

### [Objects]

It is an object of the present invention offers a method of rendering a member surface hydrophilic so that the member surface can be rendered super-hydrophilic to a contact angle with water of less than  $5^\circ$ , and maintain the hydrophilicity as long as subjected to irradiation of a UV as necessary.

### [Solving Means]

A method of rendering a member surface hydrophilic comprised of the steps of: forming on a substrate surface a mixed layer comprised of a siloxane resin (average composition formula:  $R^1_{4-n}SiO_{n/2}$  (where  $R^1$  is one kind of, or 2 kinds or more organic groups,  $1 < n < 4$ )) and titaniumoxide; and irradiating thereon a UV.

[Selected Drawing] Fig. 10